Qualitative Molecular Orbital Theory (QMOT)

The rules of QMOT

1. Consider valence AO only (e.g., for Carbon, 2s, 2p_x, 2p_y and 2p_z)

2. Form MOs for entire system as linear combination of AOs. Remember, combination of N AOs gives N MOs

3. MOs must be either symmetric or antisymmetric with respect to the symmetry operations of the molecule.

4. Compose MOs for structures of higher symmetry and then produce MOs for related but less symmetric systems by systematic distortion of the MOs of higher symmetry. For example, for the CH_2 system, start with linear HCH (D_{∞h}) then bend the system (C_2v).

5. Molecules with similar structures, such as BH_3, CH_3^+, CH_3^-, CH_3^+, NH_3, OH_3^+, have qualitatively similar MOs, the major difference is the number of electrons that occupy the common MO system.

6. The total energy of the system is a sum of the energies of occupied MOs.

7. If the two highest energy MOs of a given symmetry derive primarily from the different kinds of AOs (e.g., s and p), then mix the two MOs to form hybrid orbitals. For example, for the AH_2 system (p.3), mix C and E orbitals to form hybrid C’ and E’.
8. a) The smaller the initial energy gap between 2 interacting orbitals, the stronger the mixing
b) energy of stabilization, $e_{stab}$, is always smaller that energy of destabilization, $e_{destab}$. Thus, 4-electron-2-center interaction is always repulsive.

c) If orbitals of different energy interact (b), the one of lower energy, B, will contribute more in binding orbital; the one of higher energy, A, will contribute more in antibonding orbital.

d) The more electronegative atoms have lower energy AOs

e) The larger the overlap between interacting orbitals, the larger the interaction. $\sigma$-bonds are stronger than $\pi$-bonds.
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Walsh diagram for the $AH_2$ systems (A is a 1$^{\text{st}}$ or 2$^{\text{nd}}$ row element): the $D_{\infty h}$ to $C_{2v}$ distortion

linear $\text{CH}_2$ ($D_{\infty h}$)           bent $\text{CH}_2$ ($C_{2v}$)
Walsh diagram for the AH₃ systems (A is a 1ˢᵗ or 2ⁿᵈ row element):
  the D₃h to C₃v distortion

planar CH₃, D₃h

pyramidal CH₃, C₃v